

Effects of multiple irradiations on luminescent materials and energy savings – A case study for the synthesis of $\text{BaMO}_4: \text{Ln}^{3+}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{Ln} = \text{Eu}, \text{Tb}$) phosphors



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ABSTRACT

A novel supersonic microwave co-assistance method (abbreviated as SMC) was used to efficiently synthesize $\text{BaMO}_4: \text{Ln}^{3+}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{Ln} = \text{Eu}, \text{Tb}$) red/green phosphors at low temperature (343 K) in 40 min. X-ray powder diffraction (abbreviated as XRD), scanning electronic microscope (abbreviated as SEM) and photoluminescent spectra techniques (abbreviated as PL) were used to characterize the phosphors. SEM images revealed that shuttle shaped structures were achieved. The fluorescence property of phosphors demonstrated that both BaWO_4 and BaMoO_4 are efficient matrixes to sensitize europium or terbium. The red/green emissions were greatly enhanced under the simultaneous supersonic and microwave irradiation. We considered that this facile and effective technique owns the advantages of saving energy and shortening reaction time in contrast to conventional methods which may be promising in fabricating luminescent materials.

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1. Introduction

As far as luminescence is concerned, trivalent lanthanide ions exhibited narrow band emissions, long lifetimes and large Stokes shifts. Recent work exhibited that lanthanide doped luminescent materials were very useful in the fabrication of photovoltaic cells [1]. Additionally, they have been considered to be potential host materials for a broad range of technological applications such as phosphors, optical fibers, solid state lasers, catalysts and scintillation detectors [2].

Among numerous kinds of lanthanide containing materials, metal tungstate and molybdate have received much attention due to their distinctive scheelite-type structures crystallized in an $I4_1/a$ space group with four molecules in each crystallographic cell at ambient atmosphere. Several approaches have been proposed to assemble lanthanide activated BaWO_4 and BaMoO_4 phosphors [3,4]. However, it has to be mentioned that these methods have

different shortcomings and deficiencies. For instance, the solid state reaction will be carried out at high temperature and needs massive power supply. Although hydrothermal or solvothermal synthesis could largely reduce the reactive temperature, generally it will still be more than 373 K. Especially the reaction processes will require much longer hours (overnight). They are both considered as not energy saving or not environmentally friendly and a lot of energy and time during the preparation will be wasted. The hard or soft templates usually require pre-organization or synthesis and the results sometimes are not very stable. It is hard to control the particle size and dispersion by the relative mild technique of sol–gel treatment. Facts proved that the exploration of fabrication processes would be crucial for controlling the resultant properties of the functional materials [5,6]. Therefore, it still remains a long-standing challenge to find a more efficient method for the synthesis of lanthanide luminescent solid state materials.

Nowadays, some of the promising technique began using microwave and ultrasound as alternative energy sources for the preparation because they are mild, efficient, and energy conservation [7–9]. It is well known that microwave gains the advantages of rapid homogeneous volumetric heating and high reaction rate. Different from traditional heating, it can transfer energy directly to

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Nomenclature

SMC	supersonic microwave co-assistance
XRD	X-ray powder diffraction
SEM	scanning electronic microscope
PL	photoluminescent
FT–IR	Fourier transform infrared spectroscopy
JCPDS	Joint committee on powder diffraction standards

the reactants and induce an instantaneous internal temperature rise [10,11]. Ultrasound has been used to enhance chemical reactivity because it affects the reactive substances at a molecular level by the acoustic waves. It can produce extreme pressure and temperature variations which promoted both physical effects and chemical reactions that can directly influence the size and morphology of the products [12,13]. Thus it will be a very interesting and significant step that combines the two forces simultaneously to accelerate the targeted reactions. Based on the superiority of ultrasound and microwave, supersonic and microwave co-assistance irradiation has been proved to be an environmental friendly and efficient technique in the synthesis of semiconductor materials and specific microstructures with different morphologies have been achieved [14,15].

Up to now, no reports have been concentrated on the effects of individual radiation on the resultant materials and the internal parameters of SMC (supersonic microwave co-assistance method) method could be varied. The role and influence of the independent irradiation (within SMC treatment) on the synthesis of lanthanide containing phosphors (the current literature focused more on the preparation of semiconductors) needs to be extensively investigated. In this study, red and green phosphors $\text{BaMoO}_4: \text{Ln}^{3+}$ ($\text{M} = \text{W}, \text{Mo}$; $\text{Ln} = \text{Eu}, \text{Tb}$) were efficiently prepared via the supersonic microwave co-assistance method under very low temperature (343 K) in only 40 min. The effects of independent supersonic and microwave on crystallinity, morphology and luminescence property of products were studied in detail. Interestingly, their characteristic red/green emissions were both greatly enhanced under such a simultaneous supersonic and microwave environment. It is worth noting that this novel synthesis method owns the advantages of saving energy and shortening reaction time, which may be applied in fabricating luminescent materials in the future.

2. Materials and methods

2.1. Materials

All the chemicals were used as received without further purification. $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, Eu_2O_3 and Tb_4O_7 were provided by Aldrich company. $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ were obtained by dissolving Eu_2O_3 and Tb_4O_7 in dilute HNO_3 solution under heating with agitation.

2.2. Synthesis of $\text{BaMoO}_4: \text{Ln}^{3+}$ by SMC (supersonic microwave co-assistance method)

A typical synthesis of $\text{BaWO}_4: \text{Eu}^{3+}$ is described as follows: 20 mL of 0.1 mol/dm³ $\text{Ba}(\text{NO}_3)_2$ and 6 mL of 0.01 mol/dm³ $\text{Eu}(\text{NO}_3)_3$ aqueous solution were mixed. Subsequently, 20 mL solution containing 2×10^{-3} mol $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ was added into the above solution. The pH of the solution was maintained at 8 by the addition of ammonia. The mixture was then transferred to a three neck flask which had been adapted to fit the reactor. The supersonic assisted

microwave reactor was commercially available and produced by Nanjing Xianou technology company from China (XO-SM50) (the digital photo was presented in Fig. S1 of the supporting information). The microwave power was set as 300 W and reaction temperature remained to be 343 K. Supersonic power was 300 W with the reverse duty cycle 2 s. All the operation time were fixed as 40 min. The as-derived sample was retrieved by centrifugation at first. Then it was washed with distilled water and ethanol for three times. Finally it was dried at 333 K in vacuum.

The synthesis of $\text{BaMoO}_4: \text{Eu}^{3+}$ was simply described here: 10 mL of 0.1 mol/dm³ $\text{Ba}(\text{NO}_3)_2$ and 3 mL of 0.01 mol/dm³ $\text{Eu}(\text{NO}_3)_3$ aqueous solution were stirred together. Then 15 mL solution containing 1.43×10^{-4} mol $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ was titrated stepwise. The pH of the solution was kept to be 8.0 by the addition of ammonia. The mixture was then transferred to a three neck flask which had been adapted to fit the reactor. The microwave power was set as 300 W and reaction temperature remained to be 343 K. Supersonic power was 300 W with the reverse duty cycle 2 s. All the operation time were fixed as 40 min. The as-derived sample was obtained by centrifugation at first. Then it was washed with distilled water and ethanol for three times. Finally it was dried at 333 K in vacuum.

The sample $\text{BaWO}_4: \text{Tb}^{3+}$ and $\text{BaMoO}_4: \text{Tb}^{3+}$ were achieved by the similar procedure with the exception that $\text{Tb}(\text{NO}_3)_3$ was used as initial reactants.

2.3. Characterization of samples

The X-ray powder diffraction was investigated on a Bruker D8 diffractometer with Cu K α radiation ($\lambda = 0.1541$ nm) in the range of $2\theta = 10^\circ$ – 90° . SEM (Scanning electronic microscope) was measured with JSM-6360LV. Luminescence spectra were measured on an Edinburgh FLS920 spectrometer. Fourier transform infrared spectroscopy (abbreviated as FT–IR) results were measured within the 4000–400 cm^{−1} region on an infrared spectrophotometer (Presstinge-21) using the KBr pellet technique.

3. Results and discussion

3.1. Structural analysis

The crystallinity and phase purity of the as-prepared rare-earth ions doped BaMoO_4 ($\text{M} = \text{W}, \text{Mo}$) powders were examined with XRD (X-ray powder diffraction). Figs. 1 and 2 show the XRD patterns of $\text{BaWO}_4: \text{Ln}^{3+}$ and $\text{BaMoO}_4: \text{Ln}^{3+}$ prepared under different radiations, respectively. As can be seen in Fig. 1, all the diffraction peaks can be readily indexed to the scheelite tetragonal phase BaWO_4 (Joint committee on powder diffraction standards (named as JCPDS) card Number: 43-0646). No traces of additional peaks from other phases can be observed in the XRD patterns, which suggested that $\text{Eu}^{3+}/\text{Tb}^{3+}$ have been uniformly incorporated into the host lattice of BaWO_4 . In order to reveal the effect of different radiations, the independent parameters of SMC method have been studied and it was found that the intensity of diffraction peaks are slightly lower than expected. The sample $\text{BaWO}_4: \text{Eu}^{3+}$ or Tb^{3+} achieved by SMC method both displayed the optimal crystallinity compared with single radiation. It can be estimated that supersonic and microwave co-irradiation contributed to improve the structural orders in the solids and the crystallinity of particles has been increased.

In the case of $\text{BaMoO}_4: \text{Ln}^{3+}$, all the diffraction peaks located at 2θ values of 20° – 80° in Fig. 2 can be perfectly corresponded to the characteristic diffractions of tetragonal scheelite-type BaMoO_4 (JCPDS card No.29-0193). No peaks of any other phases or impurities were detected, indicating that the samples were phase pure and well crystallized. Similar to the XRD results of $\text{BaWO}_4: \text{Ln}^{3+}$

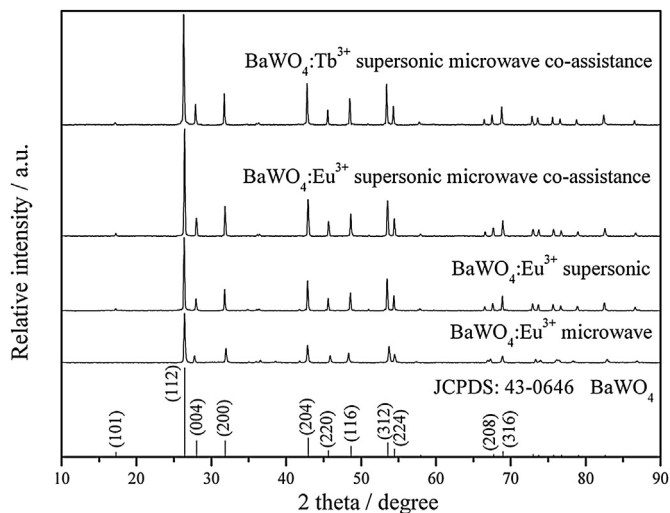


Fig. 1. XRD patterns of $\text{BaWO}_4:\text{Eu}^{3+}/\text{Tb}^{3+}$ prepared under different radiation conditions.

above, the contrast between samples synthesized under different radiation conditions also confirmed that multiple irradiations environment may contribute to the crystallization of BaMoO_4 ($\text{M} = \text{W}, \text{Mo}$) powders.

Fig. 3 shows the infrared spectra of as-prepared $\text{BaMoO}_4:\text{Ln}^{3+}$ measured in the wave number region of $400\text{--}4000\text{ cm}^{-1}$. In Fig. 3, the characteristic strong and broad absorption band around 820 cm^{-1} can be assigned to $\text{W}\text{--}\text{O}$ ($\text{Mo}\text{--}\text{O}$) dissymmetry stretching vibration deformation (ν_3) of MoO_4^{2-} (WO_4^{2-}) tetrahedron [16], confirming the presence of MoO_4^{2-} (WO_4^{2-}) groups in the product. We could clearly observe a broad band located at high frequency region and it might be derived from intense $\text{O}\text{--}\text{H}$ stretching vibration (around 3435 cm^{-1}). Two chemical species such as physically absorbed water and remaining ethanol molecules (during the washing process) may contribute to the formation of absorption signals [17]. Additional $\text{H}\text{--}\text{O}\text{--}\text{H}$ bending vibration (at 1630 cm^{-1}) was also detected.

Typical SEM micrographs of the $\text{BaMoO}_4:\text{Eu}^{3+}$ phosphor prepared by co-assistance of supersonic and microwave treatments are

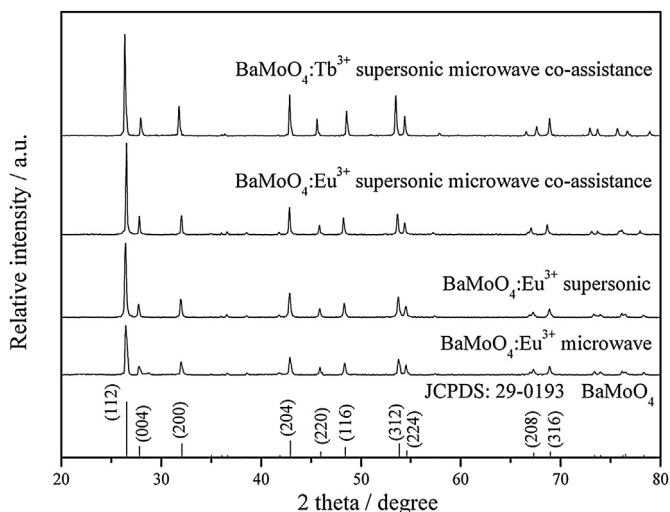


Fig. 2. XRD patterns of $\text{BaMoO}_4:\text{Eu}^{3+}/\text{Tb}^{3+}$ prepared under different radiation conditions.

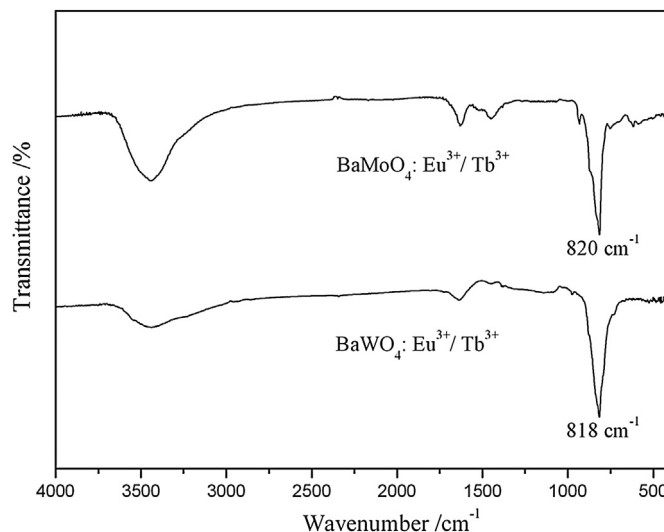


Fig. 3. FT-IR spectra of $\text{BaWO}_4:\text{Eu}^{3+}$ and $\text{BaMoO}_4:\text{Eu}^{3+}$.

shown in Fig. 4. Without template directions and excessive reaction time (hydrothermal or solvothermal), the morphology of products both exhibited the tendency to grow into regular shuttle shaped structure. In Fig. 4a–b ($\text{BaWO}_4:\text{Eu}^{3+}$), the size of the spindle like particles were $1\text{ }\mu\text{m}$ length and 400 nm width. In terms of $\text{BaMoO}_4:\text{Eu}^{3+}$ (Fig. 4c–d), the shuttle-like structure is angular and larger ($3\text{ }\mu\text{m}$ length and $10\text{ }\mu\text{m}$ width).

To investigate the effect of different radiations on the size and morphology of $\text{BaMoO}_4:\text{Eu}^{3+}$ particles, we further examined the SEM images of the microstructures prepared under single irradiation. Fig. S2a–b presents the $\text{BaWO}_4:\text{Eu}^{3+}$ phosphor synthesized under single microwave and supersonic radiation respectively. The SEM images reveal that irregular aggregated particles have been obtained under the single microwave irradiation environment (Fig. S2a). Based on the single radiation of supersonic, well dispersed polygon-shaped microparticles emerged. Only under mutual interactions of these two kinds of radiations, uniform $\text{BaWO}_4:\text{Eu}^{3+}$ shuttle shaped microparticles can be fabricated. Similar results were also observed in $\text{BaMoO}_4:\text{Eu}^{3+}$ system (Fig. S2c–d). On the basis of the analysis above, it is proposed that the crystal growth and morphology evolution of the products greatly depend on the type of irradiation environment in our experiment.

It is accepted that high temperature produced by microwave would result in good crystallinity of products while high-speed vibration aroused by supersonic might lead to the well-dispersive of microparticles. Hence, aggregation of particles would happen in terms of the microwave treatment solely. If there is only the supersonic irradiation, aggregation can be avoided. But low temperature will be related to poor crystallization. In this way, combination of microwave and supersonic irradiation owns the high temperature and optimal dispersion at the same time which maybe quite useful to the growth of crystals. Thus the simultaneous irradiations created in the SMC procedure may facilitate oriented attachment through the minimization of the surface energy. When Ba^{2+} , Eu^{3+} , and WO_4^{2-} (MoO_4^{2-}) were mixed together, bubble collapse inside the above solution aroused by high-intensity ultrasound and microwave irradiation produced intense heat and high pressure. The adjacent particles dissociated and general aggregation behavior was avoided. Consequently, shuttle shaped micro-particles could be prepared under the co-assistance of microwave and supersonic. It will be hard to achieve the similar results by single microwave or supersonic irradiation.

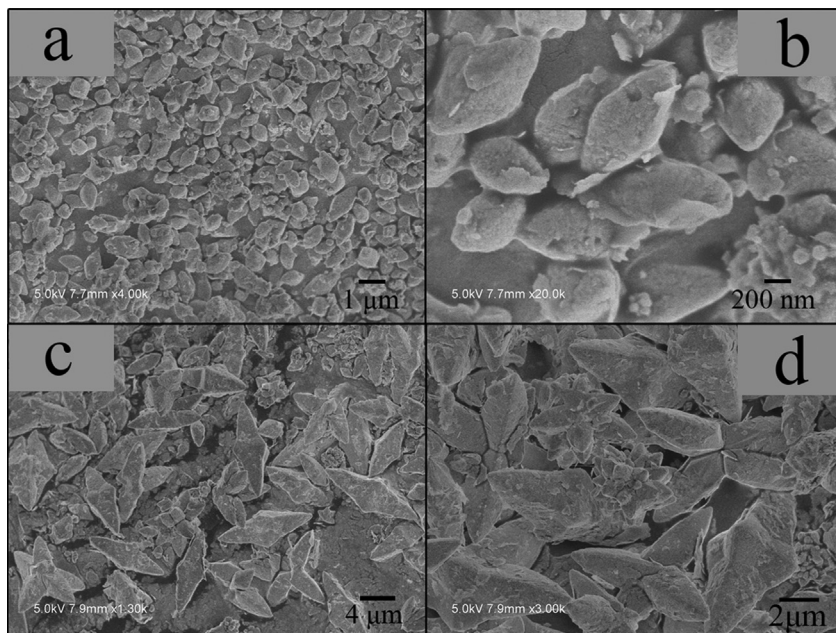


Fig. 4. SEM images of BaWO₄:Eu³⁺ (a and b) and BaMoO₄:Eu³⁺ (c and d) synthesized by SMC method.

3.2. Photophysical properties

Figs. 5 and 6 illustrate the excitation and emission spectra of the as-synthesized BaWO₄:Eu³⁺ and BaMoO₄:Eu³⁺ red phosphors. It is obvious that both BaWO₄:Eu³⁺ and BaMoO₄:Eu³⁺ exhibit strong red emission under ultraviolet (254 nm) excitation as their corresponding photographs shown (Illustrations in Figs. 5 and 6). It can be seen that BaMoO₄:Eu³⁺ (M = W, Mo) samples display similar photoluminescence spectra. The excitation spectrum of BaWO₄:Eu³⁺ was monitored at the Eu³⁺ ⁵D₀ → ⁷F₂ transition at 615 nm which consists of a broad band with the maximum at about 280 nm and some sharp peaks between 350 and 550 nm (Fig. 5). The broad band at 280 nm can be attributed to the charge transfer from oxygen to tungsten atom inside the WO₄²⁻ groups. The sharp peaks within the 4f electron configuration of Eu³⁺ can be assigned to ⁷F₀ → ⁵D₄ (361 nm), ⁷F₀ → ⁵G₂ (382 nm), ⁷F₀ → ⁵L₆ (393 nm), ⁷F₀ → ⁵D₃ (416 nm), ⁷F₀ → ⁵D₂ (464 nm) and ⁷F₀ → ⁵D₁ (536 nm). Upon excitation at 280 nm, sharp emission lines in the emission spectrum were correspond to the electronic transitions as

⁵D₀ → ⁷F₁ (592 nm), ⁵D₀ → ⁷F₂ (615 nm), ⁵D₀ → ⁷F₃ (655 nm) and ⁵D₀ → ⁷F₄ (706 nm). In terms of BaMoO₄:Eu³⁺, the broad band at 285 nm should be attributed to the charge transfer from oxygen ligands to the central molybdates atom inside the MoO₄²⁻ groups [18]. Under excitation at 285 nm, typical europium emission bands were observed. Obviously, the electric–dipole transition (⁵D₀ → ⁷F₂) located at 615 nm is the most intense and sensitive one in both BaWO₄:Eu³⁺ and BaMoO₄:Eu³⁺, indicating europium ion was in a low-symmetry coordination site. For the purpose of comparison, the effects of different radiation environments on luminescence property were examined in detail. As can be seen in Figs. 5 and 6, the phosphors BaMoO₄:Eu³⁺ (M = W, Mo) achieved under the condition of microwave and supersonic irradiation co-assistance gains the optimal red luminescence. It can be estimated the co-assistance of supersonic plus microwave irradiation accelerates the particle collisions [19] and the distances between the donor (WO₄²⁻, MoO₄²⁻) and acceptor (Eu³⁺) gets closer. Therefore efficient energy transfer rates can be achieved. In addition, the enhancement of crystallinity aroused by SMC method may also

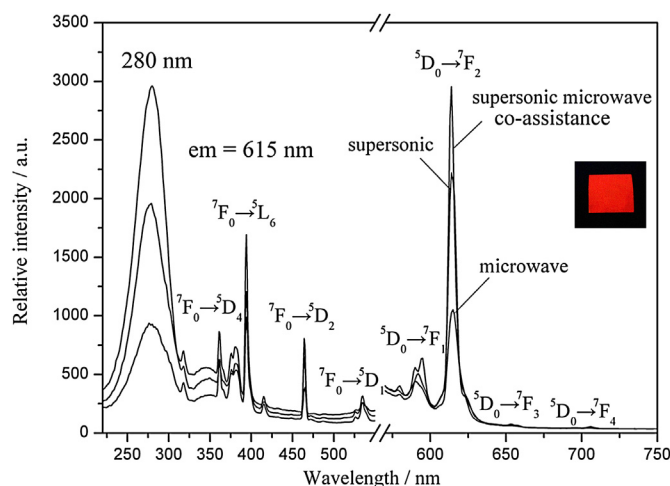


Fig. 5. Excitation and emission spectra of BaWO₄:Eu³⁺ synthesized under different radiations.

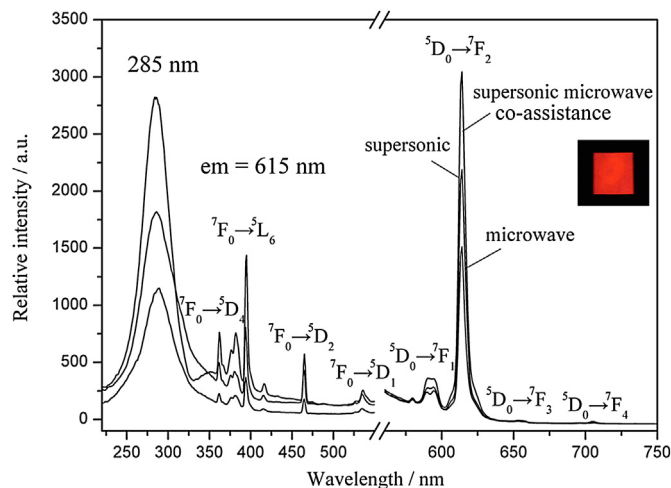


Fig. 6. Excitation and emission spectra of BaMoO₄:Eu³⁺ prepared under different radiations.

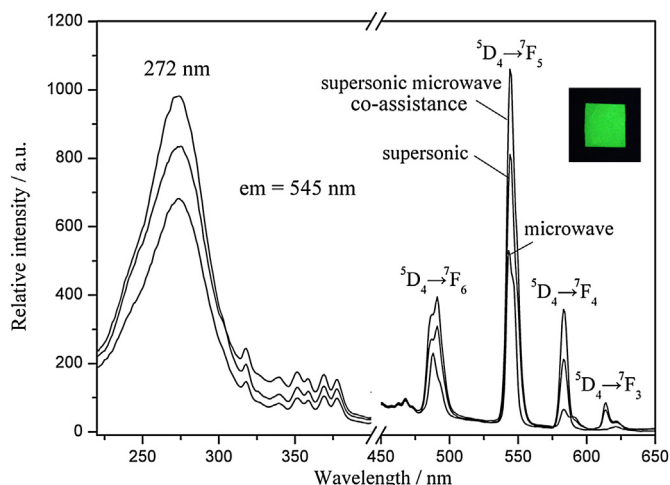


Fig. 7. Excitation and emission spectra of BaWO₄: Tb³⁺ synthesized under different radiations.

responsible for improving the luminescence intensities of Eu³⁺ in BaMoO₄: Eu³⁺ (M = W, Mo) lattices. The emission spectrum of BaMoO₄: Eu³⁺ (M = W, Mo) stimulated by longer wavelengths were also given in Fig. S3 and S4 and the characteristic red emission of Eu³⁺ were also observed under the excitation at 395 nm.

The room temperature excitation and emission spectra of the as-prepared BaMoO₄: Tb³⁺ (M = W, Mo) green phosphors were shown in Figs. 7 and 8. In Fig. 7, the observed broad band around 272 nm in the emission spectra was due to W–O charge transfer, which was similar to that in the Eu³⁺ spectrum. Upon excitation at 272 nm, multiple narrow peaks observed in the green region (490, 545, 583 and 622 nm) are transitions from the ⁵D₄ excited state to the different *J* levels of the ground state ⁷F_{*J*} (*J* = 6, 5, 4, 3), indicating the efficient energy transfer from WO₄^{2−} to Tb³⁺. Very similar photoluminescence properties can be detected in terms of BaMoO₄: Tb³⁺. The illustrations in Figs. 7 and 8 reveal that both BaWO₄: Tb³⁺ and BaMoO₄: Tb³⁺ exhibit strong red emission under ultraviolet (254 nm) excitation. In an analogous mode, we compared the effects of different radiation environments on luminescence

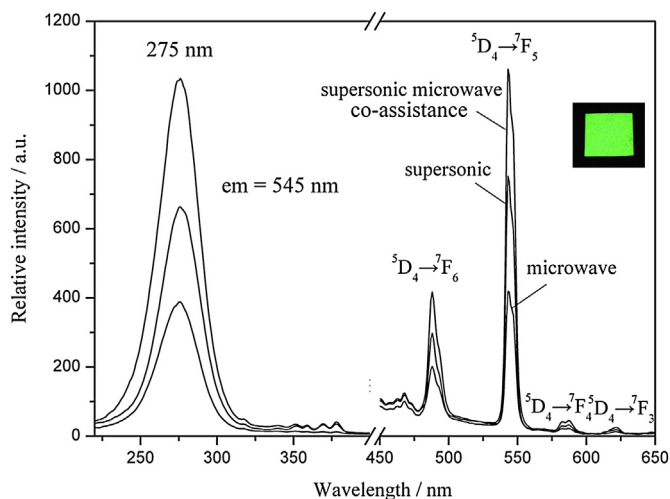


Fig. 8. Excitation and emission spectra of BaMoO₄: Tb³⁺ prepared under different radiations.

property. And it was found that SMC method was definitely the best choice to accommodate terbium(III) ions.

Based on the detailed photoluminescence analysis above, a conclusion can be drawn that both BaWO₄ and BaMoO₄ are efficient hosts to sensitize europium (red emission) or terbium (green emission). Meanwhile, SMC is more convenient and could save time for the synthesis of luminescent materials.

4. Conclusions

In conclusion, photoluminescent BaMoO₄: Ln³⁺ (M = W, Mo; Ln = Eu, Tb) were efficiently synthesized via a new SMC (supersonic microwave co-assistance method) at low temperature (343 K) within 40 min. The radiation environment was found to affect the morphology of products and shuttle shaped morphologies were finally achieved under the co-assistance of microwave and supersonic. The obtained BaMoO₄: Eu³⁺ and BaMoO₄: Tb³⁺ exhibited the characteristic red and green emission which demonstrated that there existed significant energy transfers from WO₄^{2−} (MoO₄^{2−}) groups to Eu³⁺ and Tb³⁺. Further comparisons illustrated that the sample prepared by SMC method own the optimal fluorescence performance. As a new approach of synthesis of luminescent materials, SMC is more convenient and saves time which might be widely used in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.energy.2013.11.026>.

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